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Evaluation of slag and fly ash for high volume cement replacements using ternary blended concrete and lime activation

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The Degree of Master of Technology

भारतीय प्रौद्योगिकी संस्थान हैदराबाद

Indian Institute of Technology Hyderabad

Department of civil Engineering

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Declaration

I declare that this written submission represents my ideas in my own words. and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

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Approval Sheet

This thesis entitled **Evaluation of slag and fly ash for high volume cement replacements using ternary blended concrete and lime activation** by Faraz Tariq is approved for the degree of Master of Technology/ Doctor of Philosophy from IIT Hyderabad.

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Dedicated to

My mother.

Abstract

Supplementary cementitious materials (SCMs) such as fly ash (FA) and slag are being increasingly used in cement and concrete due to environmental, economical, and concrete quality-related concerns.

By combining the reactivity, workability and water reduction of the lower priced fly ash with the reactivity of slag that allows for greater Portland cement replacement, more economical, high quality concrete can be produced.

In this work, the possibility of replacing high volumes of cement was explored by using by product supplementary cementitious materials such as fly ash, ground granulated blast furnace slag (GGBFS). The volume of cement replaced was 70% using different proportions of fly ash and slag in eight different mixes. The proportions of fly ash and slag tried in this study were varied from 0 to 70%. Eight Mixes in total were prepared, out of which two were binary blends and rest were ternary mixes. Binary blends were comprised of cement with fly ash or cement with slag while ternary mixes were composed of both fly ash and slag in combination with 30% cement. The cubes of all the eight mixes were tested for compressive strength at appropriate ages and the details were reported accordingly. The other objective of this study was the monitoring of the hydraulic or pozzolanic reaction going on in the system by determining the water contents and available calcium hydroxide in the hydrating systems. For this purpose, the option of Thermo-gravimeteric analysis TGA was undertaken at appropriate ages by preparing mixes in the same manner without adding the aggregates to the pastes. It was observed that some of the systems, especially those consisting high amount of fly ash were lacking in Calcium hydroxide. Therefore it was decided to activate the systems by lime addition. The addition of lime was aimed to increase the alkalinity of the system at the same time to provide lime to the fly ash available in the system for initiating the pozzolanic reaction. The results of compressive strength were better than those obtained without activation especially for fly ash systems whereas for slag mixes, there was no noticeable effect of activation. The performance of ternary blends was best among all and also improved to a little extent. The binary mixes of slag also performed well almost uniformly irrespective of the lime activation dosages. reaction For instance, use of 25% slag and 25% fly ash provide lower coefficient of permeability than 50% fly ash or 50% slag (fly-ash-slag-recycled aggregate-blend, miadata 16). Very little work has been reported in the literature on the ternary blends with high volume slag and fly ash replacement and the little information available suggests low reactivity.

Both fly ash and slag rely on the excess lime/calcium hydroxide from Portland cement that is found in hardened concrete. This non-durable, water-soluble material called efflorescence is visible as a white chalky deposit on the surface of concrete. Fly ash and slag combine with the calcium hydroxide to create the same durable calcium-silica-hydrate (CSH) “glue” as Portland cement. This reaction is a slower, long-term reaction that will increase long-term concrete strength and reduce concrete permeability, thereby increasing the durability of concrete.

Nomenclature

C…………….CaO

S……………..SiO_2

H……………..H_2O

C-S-H………..Calcium silicate hydrate

FA……………Fly ash.

GGBFS………Ground granulated blast furnace slag.

Mix designations.

Name of the mix	**Cement content**	**Slag content**	**Fly ash content**
Control, C	100%	0%	0%
Mix M1	30%	35%	35%
Mix M2	30%	70%	0%
Mix M3	30%	10%	60%
Mix M4	30%	60%	10%
Mix M5	30%	20%	50%
Mix M6	30%	50 %	20%
Mix M7	30%	0%	70%

Lime addition mixes designations.

MIX	**Proportion**
Control C	100% cement
M1-C	30+35+35 with 0% lime
M1-5P	30+35+35 with 5% lime
M1-10P	30+35+35 with 10% lime
M1-15P	30+35+35 with 15% lime
M2-C	30+70+0 with NO lime
M2-5P	30+70+0 with 5% lime
M2-10P	30+70+0 with 10% lime
M2-15P	30+70+0 with 15% lime
M7-C	30+0+70 with NO lime
M7-5P	30+0+70 with 5% lime
M7-10P	30+0+70 with 10% lime
M7-15P	30+0+70 with 15% lime

Contents

Chapter 1

Introduction

Supplementary cementitious materials (SCMs) such as fly ash (FA) and slag are being increasingly used in cement and concrete due to environmental, economical, and concrete quality-related concerns. Concrete practice has shown that the performance of concrete containing SCMs, such as workability, entrained air stability, set time, and strength development, significantly varies with the sources or characteristics of the cementitious materials, SCM replacement levels, and weather conditions. Concrete containing SCMs often displays slow hydration that is accompanied by slow setting and low early age strength. This effect is more pronounced as the level of SCM replacement is increased.

Use of mineral admixtures or supplementary cementitious materials (SCM) has been explored to improve specific aspects of concrete performance. Blended cements, which are essentially binary blends of cement and SCMs have been used. However, the use of one SCM may not provide the required performance characteristics. While binary blends improve specific aspects of performance, the overall performance is not improved since other properties are compromised. For instance, silica fume is known to provide enhanced strength gain and reduced permeability, however, is extremely prone to restrained shrinkage cracking. Silica fume, especially in low water to cement systems produces autogenous shrinkage and has a very high heat release. Similarly, it is shown that fly ash reduces potential for restrained shrinkage cracking, but its low reactivity is a major hindrance to the development of concrete consisting of large volumes of fly ash. It is increasingly becoming evident that use of single SCM is not sufficient. The solution lies in using ternary blends where the beneficial effects of one or more SCMs can be harnessed.

Ternary blends allow greater flexibility in achieving properties where potential benefits from two SCMs are realized simultaneously with possible synergistic effects. Ternary blends comprising of slag and fly ash offer an economically attractive solution, which can lead to high performance concrete. Concrete produced with a combination of slag, fly ash and Portland cement has proven to enhance concrete performance by producing higher long-term strength, improving workability, while requiring less water while reducing efflorescence and permeability. Some synergy has also been reported. For instance,use of 25% slag and 25% fly ash provide lower coefficient of permeability than 50% fly ash or 50% slag (fly-ash-slag-recycled aggregate-blend). Very little work has been reported in the literature on the ternary blends with high volume slag and fly ash replacement and the little information available suggests low reactivity. Such a system would therefore require activation. The activation of slag and fly ash using external agents is a promising method to overcome this low reactivity.

In this thesis, high volume cement replacement with slag and fly ash is investigated. The objectives of the work reported here is not just to test ternary blends of slag and fly ash, but to, develop an understanding of the role of each component and its contribution to a performance characteristic of concrete. Compressive strength gain in ternary blends with 70% cement replacement is investigated. Finally, the use of lime activation in enhancing the strength gain in slag and fly ash for high volume cement replacement is explored.

1.1 Objectives

The objectives of the work reported in this thesis are:

1. To investigate the compressive strength gain in concrete with high volume cement replacement ternary blend of slag and fly ash.
2. To investigate the contribution of fly ash and slag to strength gain at different ages in ternary blended cement
3. To explore the role activation in enhancing the strength gain in concrete containing high volume cement replacement with fly ash and slag

1.2 Organization of thesis

This thesis is organized in five chapters. Description of content of each chapter is given below

Chapter 2

It presents literature review on the characteristics and performance of supplementary cementitious materials like fly ash and GGBF slag. Their specifications, compositions, reactions and performance characteristics under various conditions have been summarized. Another aspect covered in this chapter gives the literature review of alkaline activation of the pozzolanic and supplementary cementitious materials including the effect of different activators on early as well as later ages of concrete proportioned with supplementary cementitious materials replacing high volume of cement has been covered.

Chapter 3

It describes the materials used in this work and methods followed to execute the work as well as the characteristics properties of materials and results of tests done to validate the materials according to the specifications of Indian standards

Chapter 4

It covers the description of work done in the first half of this project on ternary blended concrete with high volume cement replacement in the light of high volume fly ash and slag concrete with the results obtained with analysis of the data and observations and inferences drawn in accordance with the related work done by researchers previously and available literature.

Chapter 5

It presents the results,observations and conclusions based on lime activation part of the study and inferences drawn on the basis of the results obtained through various modes in the light of characteristics of materials used as well as available literature and the similar work done on the topic by the researchers previously.

Chapter 2

Literature review

2.1. Introduction

The use of materials such as fly ash as a supplementary cementing material in concrete has become common these days. Properly used, fly ash can significantly enhance the properties of concrete. There is increasing concern among researchers to replace higher amounts of Portland cement with fly ash to help reduce the CO_2 emissions associated with the manufacturing of Portland cement. Essentially, for every tonne of Portland cement manufactured, one tonne of CO_2 is released into the atmosphere. The total worldwide environmental release of CO_2 in 1998 was estimated at 23 billion tonnes, with Portland cement production accounting for approximately 7% of the total carbon dioxide emissions (Mehta, 1999). Therefore, replacing Portland cement with fly ash could reduce cement production and hence reduce CO_2 emissions. The current annual worldwide production of fly ash is approximately 500 million tonnes, but only approximately 20% is being used by the cement and concrete industry (Mehta, 1999). The demand and consumption of Portland cement is increasing, therefore it is important for the cement and concrete industry to start utilizing more fly ash to meet these demands rather than increase Portland cement production (Malhotra and Mehta, 2002).

Fly ash reacts in concrete with the hydraulic cement in the following ways

1. Solutions of calcium and alkali hydroxide, which are released into the pore structure of the paste, combine with the pozzolanic particles of fly ash, forming a cementing medium; and

2. Heat generated by hydration of hydraulic cement helps initiate the pozzolanic reaction and contributes to the rate of the reaction.

If concrete containing fly ash is properly cured, the products of reaction of flyash partially fill in the spaces initially occupied by mixing water that were not filled by the hydration products of the cement, thereby reducing the concrete permeability to water and aggressive chemicals (Manmohan and Mehta 1981). The reaction rate of fly ash is slower, as compared to hydraulic cement, which reduces the amount of early heat generation and the detrimental early temperature rise in massive structures.

Concrete containing fly ash can achieve properties that are not achievable through the use of hydraulic cement alone. Extensive research has been done to improve the understanding of the chemical reactions involved when fly ash is used in concrete.Strength enhancement characteristics of a fly ash vary widely, depending on the physical and chemical properties of the ash and the general characteristics of the cement in which it is used. The properties that are commonly controlled by beneficiation processes are fineness and loss on ignition (LOI), an indicator of carbon content. Depending on the size, density, and distribution of particles containing carbon, the LOI can be increased, decreased, or unchanged by this technique. In general, the finer the fly ash, the lower the LOI and the greater the concrete’s long-term compressive strength. Increased fineness also lowers the water demand and increases resistance to sulfate attack in concrete.

Fly ash contains heterogeneous combinations of amorphous (glassy) and crystalline phases. The largest fraction of fly ash consists of glassy spheres of two types: solid and hollow (cenospheres). These glassy spheres usually make up 60 to 90% of the total mass of fly ash, with the remaining fraction of fly consisting of a variety of crystalline phases.ASTM C 618 categorizes fly ash by chemical composition, according to the sum of the iron, aluminum, and silicon content (expressed in oxide form). As a group, Class F and C ashes generally show different performance characteristics; however, the performance of a fly ash is not determined merely by its classification.

The ASTMcharacterization is used as a quality-control or quality-assurance tool. Although the chemical composition of fly ash is reported as oxides however the constituents of fly ash are not normally present as oxides. The crystalline and glassy constituents that remain after the combustion of the pulverized coal are a result of materials with high melting points and incombustibility. The amounts of the four principal constituents vary widely as shown in the table below.

Table 2.1.Typical composition of fly ash.

SiO_2	**35 to 62**
Al_2O_3	**10 to 30**
CaO	**1 to 35**
Fe_2O_3	**4 to 20**

The sum of the first three constituents (SiO_2, Al_2O_3, and Fe_2O_3) must exceed 70% for a fly ash to be classified as an ASTM C 618 Class F fly ash; whereas their sum must only exceed 50% to be classified as an ASTM C 618 Class C fly ash. Class C fly ashes generally contain more than 20% of material reported as CaO; therefore, the sum of the SiO_2, Al_2O_3, and Fe_2O_3 may be significantly less than the 70% Class F minimum limit.

The main contributor to the pozzolanic reaction in concrete is the siliceous glass from the fly ash because it is the amorphous silica that combines with lime and water to form calcium silicate hydrate (C-S-H), the binder in concrete.

Fly ash consists largely of small glassy spheres that form when the burned coal residue cools very rapidly. The composition of the pulverized coal and the temperature at which it is burned determines the composition of these glasses. The glass content of fly ash and glass composition strongly determines its reactivity. The fly ash containing high calcium or high-alkali glasses exhibithigher reactivity at early ages than low-calcium or low-alkali fly ashes, although this should be evaluated on a case-by-case basis.

The properties of freshly mixed, unhardened concrete are highly influenced by shape, size, particle-size distribution of fly ash, while density of fly ash particles influence, and the strength development and other properties of hardened concrete. This is due in part to the influence of particle characteristics on the water demand of the concrete mixture.

2.2. Chemical activity of fly ash in hydraulic cement concrete

The principal product of the reactions of fly ash with calcium hydroxide and alkali in concrete is calcium silicate hydrates (C-S-H)and calcium aluminate hydrates which is the same as thatof the hydration of Portland cement. The reaction of fly ash depends largely on breakdown and dissolution of the glassy structure by the hydroxide ions and the heat generated during the early hydration of the hydraulic cement fraction. The fly ash continues to consume $CaOH_2$ to form additional C-S-H, as long as $CaOH_2$ is present in the pore fluid of the cement paste and as long as there is available mixing water filling space that the C-S-H can occupy; at $w/cm < 0.4$ by mass, there will be more space available before all cementitious material react (Philleo 1991). Regourd et al. (1983) state that a very small, immediate chemical reaction also takes place when fly ash is mixed with water, preferentially releasing calcium and aluminium ions to solution. This reaction is limited, however, until additional alkali or calcium hydroxide or sulphates are available for reaction. Idorn (1984) has suggested that, in general, fly-ash reaction with Portland cement in modern concrete is a two-stage reaction.Initially and during the early curing, the primary reaction is with alkali hydroxides and, subsequently, the main reaction is with $CaOH_2$.

The effectiveness of the use of fly ash in concrete depends on the following factors.

1. The chemical and phase composition of the fly ash and of the hydraulic cement;
2. The alkali-hydroxide concentration of the reaction system;
3. The morphology of the fly ash particles;
4. The fineness of the fly ash and of the hydraulic cement;
5. The development of heat during the early phases of the hydration process; and
6. The reduction in mixing water requirements when using fly ash.

2.3. Compressive strength and rate of strength gain

The strength at a given age as well as the rate of strength gain of fly ash concrete are affected by the characteristics of the particular fly ash, the cement with which it is used, and the proportions of each used in the concrete (EPRI CS-3314). As compared to the concrete without fly ash proportioned for equivalent 28-day compressive strength, concrete containing a Class F fly ash may develop lower strength at 7 days or less when tested at room temperature (Abdun-Nur 1961). By using accelerators, activators, water reducers, or by changing the mixture proportions, equivalent 3- or 7-day strength may be achieved (Bhardwaj, Batra, and Sastry 1980; Swamy, Ali, and Theodorakopoulos 1983; Dhir, Zhu, and McCarthy 1998; Shi and Qian 2000).

After the rate of strength gain of hydraulic cement slows, the continued pozzolanic reaction of fly ash provides strength gain at later ages if the concrete is kept moist; therefore, concrete containing fly ash with equivalent or lower strength at early ages may have equivalent or higher strength at later ages than concrete without fly ash. This strength gain continues with time and results in higher later-age strengths than can be achieved by using additional cement (Berry and

Malhotra 1980). Lane and Best (1982) have reported strength increases of 50% at 1 year for concrete containing fly ash, as compared with 30% for concrete without fly ashusing 28-day strengths as references.

2.4. High-volume fly ash concrete

HVFA concrete may be defined as having a fly ash content of 50% or greater by mass of cementitious materials. Ramme and Tharaniyil (2000) described concrete with 37% fly ash as being HVFA. HVFA concrete can be considered to represent concrete containing higher percentages of fly ash than normal for the intended application of the concrete. This has a low *w/cm* content and is batched to a dry consistency. Several researchers have reported on development of HVFA concrete of moderate to high slumps using high-range water-reducers and possessing suitable properties for commercial construction. Mehta (1999) discussed CO_2 and the role it plays in global warming and emphasized on the need to increase consumption of mineral admixtures to help reduce the production of CO_2. Mehta and Burrows (2001) further discuss the role HVFA concrete can play in concrete to gain durability.

2.5. Ground granulated blast furnace slag

A non-metallic product, consisting essentially of silicates and alumino-silicates of calcium and of other bases, that is developed in a molten condition simultaneously with iron in a blast furnace. Granulated blast-furnace slag is the glassy granular material formed when molten blast-furnace slag is rapidly chilled, as by immersion in water. During the extraction of iron from ores, blast furnace is continuously charged from the top with iron oxide (ore, pellets, sinter,etc.), fluxing stone (limestone and dolomite), and fuel (coke). Both are periodically tapped from the furnace at a temperature of about 1500 C.

The ranges in composition from source to source shown in Table 2.2 are much greater than those from an individual plant. Modern technology produces blast-furnace slag with a very low variability in the compositions of both the iron and the slag from a single source.To increase the hydraulic (cementitious) properties, the molten slag must be cooled or chilled rapidly as it leaves the blast furnace. Rapid quenching minimizes crystallization and converts the molten slag into fine-aggregate-sized particles (generally smaller than a 4.75 mm (No. 4) sieve, composed predominantly of glass. This product is referred to as granulated iron blast-furnace slag. The cementitious action or hydraulicity of a granulated blast-furnace slag depends to a large extent on the glass content, although other factors also have some influence. Slowly cooled slags are mostly in crystalline form and therefore do not possess significant cementitious properties.

Table _Typical chemical composition of GGBFS

SiO_2	**32 to 42**
Al_2O_3	7 to 16
CaO	32 to 45
MgO	5 to 15
S	0.7 to 2.2

Fe_2O_3	0.1 to 1.5
MnO	0.2 to 1.0

ASTM C 989, provides three strength grades of GGBF slags, depending on their respective mortar strengths when blended with an equal mass of portland cement. The classifications are Grades 120, 100, and 80,* based on the slag-activity index expressed as a ratio of average compressive strength of slag-reference cement mortar cubes to average compressive strength of reference cement mortar cubes.

The principal hydration product which is formed when GGBF slag is mixed with Portland cement and water is basically the same as the principal product formed when Portland cement hydrates, i.e., calcium-silicate hydrate (C-S-H). GGBF slag hydrates are generally found to be more gellike than the products of hydration of Portland cement, and therefore increase the density of the cement paste.

When GGBF slag is mixed with water, initial hydration is comparatively slower than Portland cement mixed with water; therefore, the activators with Portland cement or alkali salts or lime are used to increase the reaction rate. The reaction of GGBF slag in the presence of Portland cement is dependent largely upon breakdown and dissolution of the glassy slag structure by hydroxyl ions released during the hydration of the Portland cement. In general, the GGBF slag reacts with alkali and calcium hydroxide $Ca(OH)_2$ to produce additional CSH. Regourd (1980) reported that a very little immediate reaction also takes place when GGBF slag is mixed with water, preferentially releasing calcium and aluminium ions to solution. Initially and during the early hydration, the reaction is mainly with alkali hydroxide, but subsequent reaction is predominantly with calcium hydroxide.

2.6. Factors determining cementitious properties

The primary factors influencing the effectiveness GGBF slag in hydraulic cement are:

a) Chemical composition of the GGBF slag.

b) Alkali concentration of the reacting system.

c) Glass content of the GGBF slag.

d) Fineness of the GGBF slag and Portland cement.

e) Temperature during the early phases of the hydration process.

2.6. Proportioning with GGBF slag

In most cases, GGBF slags have been used in proportions of 25 to 70 percent by mass of the total cementitious material. These proportions are in agreement with those established by ASTM C 595 for the production of Portland blast-furnace slag cement. The quantity of GGBF slag is generally decided by the purposes for which the concrete is to be used, the curing temperature, the grade (activity) of GGBF slag, and the Portland cement or other activator. In case of blended cements, the combination of cementitious material will result in physical properties that are characteristic of the predominant material. For example,a slower rate of strength gain is expected, particularly at early ages, with the increasing percentage of GGBF slag, unless the water content is considerably reduced or accelerators are used or accelerated curing is provided. GGBF slags are usually substituted for Portland cement on a one-to-one basis by mass and are always considered in the determination of the water to cementitious material ratio. Water demand for given slump may generally be 3 to 5 percent lower than that found with concrete without GGBF slag (Meusel and Rose 1983).

Ternary system usually refers to the use of GGBF slag in combination with Portland cement and pozzolans such as fly ash and silica fume. Typically the use of a ternary system is for economic reasons, but it may also be used for improving engineering properties.Among the other effects, silica fume is often added to proportion ternary systems toachieve increased strength and reduced permeability. In addition, GGBF slag has been used in combination with Portland cement and ground quartz (silica flour) in autoclaved concrete masonry (Hooton and Emery 1980).

2.7. Strength and rate of strength gain

Compressive and flexural strength-gain characteristics of concrete containing GGBF slag can vary over a wide range. When compared to Portland cement concrete, use of Grade 120 slag typically results in reduced strength at early ages (1 to 3 days) and increased strength at later ages (7 days and beyond) (Hogan and Meusel 1981). Use of grade 100 slag results in lower strength at early ages, (1 to 21 days) but equal or greater strength at later ages.Grade 80 gives reduced strength at all ages. The extent to which GGBF slags affect strength depends on the slag activity index of the particular GGBF slag, and the proportions in which it is used in the mixture indicates that the mortar strength potential of 50-percent blends is dependent upon the grade of GGBF slag as defined in ASTM C 989.

Other factors affecting the performance of GGBF slag in concrete are water-cementitious materials ratio, physical and chemical characteristics of the Portland cement, and curing conditions. The percentage of strength gain achieved with a Grade 120 GGBF slag is greater in concrete mixtures which have high water-cementitious materials ratio than in mixtures with a low water-cementitious materials ratio (Fulton 1974; Meusel and Rose 1983). The same trend was also noted by Malhotra (1980).

2.8. Chemical activation of fly ash cementitious systems

The coal fly ash as a cement replacement in concrete is the very common and attractive because of its high volume utilization and widespread construction. However, the use of fly ash is also accompanied by increased setting time and decreased early strength.Most of the researchers are of the opinion that early age strengths of concretes with partial replacement of cement by fly ash are reduced. As fly ash qualitatively is not equivalent to Portland cement,this reduction in strength occurs due to high water-cement ratio.

Different methods, such as fine grinding, elevated temperature curing and use of chemical activators, have been explored to overcome theseshortcomings. Aftercomparative studies,it has been found that the use of chemical activator is the most effective and efficient technique to activate the potential pozzolanic reactivity of coal fly ashes and to improve the performance of the fly ash in concrete.

Some researchers have suggested that by addition of an alkali activator, pozzolanic reaction of such concretes at early ages can be accelerated. Shi (2008) has described the results of an experimental study wherein the addition of an alkali activator to accelerate the early hydration of binder in a fly ash concrete and lime addition in order to maintain the supply of calcium hydrate at later ages.

The activation of potential cementitious property of blast furnace slag and pozzolanic reactivity of pozzolans by the use of chemical activators has been found to be quite effective. The mechanism activation can be briefly summarized as follows.The addition of $CaCl_2$ inhibits the solubility of $Ca(OH)_2$ and hence decreases the pH of pore solution due to the common ion effect, which decreases the dissolution of fly ash, but favours the formation of a solid solution of $Ca_4Al_2[(SO_4\ 2\text{-})X(Cl\text{-}\ )Y(OH\text{-})_2\text{-}2X\text{-}Y].nH_2O$ ($X<1$ and $Y<2$). The formation of the solid solution increases the dissolution of fly ash particles and the pozzolanic reaction, which enhances the strength of fly ash cement and concrete.

The addition of Na_2SO_4 to fly ash cement accelerates the pozzolanic reaction between lime and fly ash by increasing the alkalinity of the solution and the dissolution of fly ash during initial stages. Also it results in the formation of more ettringite, which results in a significant solid volume increase, a less porous structure and higher strength.

The addition of chemical activator(s) can significantly enhance the rate pozzolanic reactions between fly ash and lime, and hence increase the strength development rate and ultimate strength of hardened concrete containing fly ash. Chemical activator(s) can be easily added into concrete mixtures during the concrete mixing process. Both Na_2SO_4 and $CaCl_2.2H_2O$ are effective in activating the reaction of fly ash and increasing strength concrete containing a high volume of fly ash. Na2SO4 is more effective at early ages and $CaCl_2.2H_2O$ at later ages

2.9. Early Microstructure Development in Activated Fly ash

In this research work, a sub bituminous ASTM C 618class F fly ash was used. Chemical reagents Na_2S0_4 and $CaC1_2.2H_20$ were used as activators. A commercial hydrated high calcium lime was blended with fly ash to test the pozzolanic reactivity of fly ash.

Pozzolanic reactivity and the nature of hydration products of the fly ash was tested by blending 80% fly ash and 20% hydrated lime in mass. To produce a paste with a normal consistency,a water to solid ratio of 0.35 was used. Activators Na_2SO_4 and $CaC1_2.2H_20$, with the dosage of 4% based on the mass of lime-fly ash blend were used.

XRD patterns in combination with the SEM observations showed that C-S-H gel was the main hydration product in the three pastes. The addition of activator changed the nature of other hydration products.In addition to C-S-H, ettringite (AFt) and AFm were found to be formed in the control pastes. The amount of AFt was minor without any noticeable change from 3 to 28 days. While AFm diffraction peaks were intensified from 3 to 28 days. Unreacted hydrated lime was also detected and its diffraction was unchanged from 3 to 28 days.

The addition of Na_2S0_4 increased both early and later strengths of lime-fly ash pastessignificantly. The effect of $CaCl_2$on strength gain was less at 3 and 7 days, but more pronounced at 28 days than Na_2S0_4. A suggested activation mechanism of lime-fly ash pastes by Na_2S0_4 and $CaC1_2$ can be briefly described in the following paragraphs.

The addition of Na_2S0_4 to lime-fly ash pastes increases the alkalinity of the solution and the dissolution of fly ash at initial stages The initial dissolution of fly ash governs the early pozzolanic reaction which accelerates the pozzolanic reaction between lime and fly ash. At the same time, significant amount of AFt is also formed possibly due to the added $S0_4$. The accelerated initial pozzolanic reaction and the subsequent formation of Aft contribute to high early strength of the lime-fly ash paste. As time proceeds, pozzolanic reaction continues and pastes become stronger.

Chapter 3

Materials and experimental methods

3.1 Introduction

This section presents the details of materials and experimental methods used in the study. The types of specimens, mix proportions and test methods employed are presented.

3.1.1 Cement

In the present investigation, a commercially available 53 grade ordinary Portland cement conforming to is 8112 (1989) was used for all concrete mixtures. The cement properties are listed in Tables 1 and 2.

Table 1: Properties of Cement tested as per IS: 4031

TEST PARAMETERS	Unit of Measurement	RESULTS	Requirements as per IS: 3812
Normal consistency	%	30	
fineness	m^2/kg	328	min 225
initial setting	min	200	min 30
final setting	min	275	max 600
soundness			
1. Le-Chatilier	mm	0.5	max 10
2. autoclave	%	nil	max 0.8
compressive strength			
1. 3 day	MPa	29	27
2. 7 days	MPa	38.5	37
3. 28 days	MPa	55	53

Table 2: Properties of Cement tested as per IS: 4032-1985

Test conducted	Unit of Measurement	RESULT	Requirement as per IS: 12269
Total loss on ignition	% by mass	1.53	Not more than 4
Insoluble residue	% by mass	0.99	Not more than 3
Ratio of % of lime to % of silica, alumina & iron oxide when calculated by the formulae: $(CaO-0.7\ SO_3)/(2.8*SiO_2+1.2*Al_2O_3+0.65*Fe_2O_3)$	% by mass	0.89	Not more than 1.02 & not less than 0.8
Ratio of % of alumina to iron oxide		1.24	Not less than 0.66
Total sulphur content calculated as sulphuric anhydride (SO_3)	% by mass	2.24	Not more than 2.5% for C3A less than 5% and Not more than 3% for C_3A greater than 5%

Magnesia (MgO)	% by mass	1.28	Not more than 6%
Tricalcium Aluminate (C_3A)	% by mass	7.46	

3.1.2 Aggregates

Locally available crusher sand with a specific gravity of 2.65 and fineness modulus of 2.7 was used as fine aggregate and crushed granite of specific gravity of 2.78 was used as coarse aggregate. Two different classes of coarse aggregate fractions were used: 10-4.75 mm and 20-10 mm. The aggregate properties are listed in Tables 3 and 2.

Table 3: Physical properties of 20 mm coarse as per IS: 2386 (1963) and IS: 383 (1963)

Test parameter	Unit of Measurement	RESULT
Loose Bulk density	Kg/Lit	1.44
Compacted Bulk density	Kg/Lit	1.57
water absorption	%	0.5
Specific gravity		2.69
Deleterious material	%	0.21
crushing value	%	17.25
Load required to 10% fines	Tons	27

Table 4: Physical properties of 10 mm coarse aggregate as per IS: 2386 (1963) and IS: 383 (1963)

Test parameter	Unit of Measurement	RESULT
Loose Bulk density	Kg/Lit	1.34
Compacted Bulk density	Kg/Lit	1.5
water absorption	%	0.6
Specific gravity		2.65
Deleterious material	%	0.17
crushing value	%	17.08
Load required to 10% fines	Tons	27

Table 5: Physical properties of fine aggregate as per IS: 2386 (1963) and IS: 383 (1963)

Test parameter	Unit of Measurement	RESULT
Loose Bulk density	Kg/Lit	1.54
Compacted Bulk density	Kg/Lit	1.64
water absorption	%	1.4
Specific gravity		2.58

Deleterious material	%	3

Table 6: Physical properties of dust aggregate as per IS: 2386 (1963) and IS: 383 (1963)

Method of testing: IS: 2386, IS: 383,

Test parameter	Unit of Measurement	RESULT
Loose Bulk density	Kg/Lit	1.69
Compacted Bulk density	Kg/Lit	1.82
water absorption	%	3.5
Specific gravity		2.69
Deleterious material	%	14.25

Table 6: Gradation of fine aggregate

Sieve size (mm)	**% passing**	**Standard Grading limits**
	100%	**IS: 383 - 1970**
10 mm	100	100
4.75 mm	98	90-100
2.36 mm	83.6	75-100
1.18 mm	59.2	55-90
600 micron	39.6	35-59
300 micron	17.6	08--30
150 micron	8	0-10

Note: As per IS 383 Table 4 for crushed sand stones the permissible limit on 150 micron sieve is increased to 20 percent.

Table 7: Gradation of coarse aggregate

	% passing	
Sieve size (mm)	Fraction I - 20mm	Fraction II - 10mm
20 mm	92.38	100
10 mm	8.00	97
4.75 mm	2.25	14.3
2.36 mm	0	4

Table 8:Gradation of combined coarse aggregate

	Coarse aggregate fractions		Combined grading	Table 2 of
Sieve size (mm)	20mm	10mm		Grading limits
	60%	40%	100%	IS: 383 - 1970
40 mm	100	100	100	100
20 mm	92.38	100	95.43	95-100

10 mm	8.00	97	43.60	25-55
4.75 mm	2.25	14.3	7.07	0-10

3.1.3 Fly Ash

Fly ash conforming to the requirements of IS 3812 and IS 1727 (1967) from the Ramagundam thermal power plant was used as a supplementary cementitious material in concrete mixtures. The properties of the fly ash are shown in Tables 9 and 10 below.

Table 9 Chemical characteristics of fly ash as per IS: 1727 1967

TEST CONDUCTED	**Unit of Measurement**	Results	Requirement as per IS: 3812
Sulfur dioxide + Aluminum oxide + Iron oxide	% by mass	93.84	not less than 70%
Sulphur dioxide	% by mass	61.37	not less than 35%
Magnesium oxide	% by mass	0.95	max. 5%
total Sulphur as Sulphur trioxide	% by mass	0.19	max. 5%
available alkalis Na_2O	% by mass	0.005	max. 1.5%
Chloride	% by mass	0.003	max. 0.05%
loss on ignition	% by mass	0.61	max. 5%

Table 10: Properties of fly as per 3812 (Part 1 and 2) : 2003

	Unit of Measurement	RESULTS	Requirement as per IS: 3812
lime reactivity	MPa	7	min. 4.5
Fineness	m^2/kg	255	min. 200
compressive strength as a percentage of cement mortar cubes	%	92	more than 80%
Soundness as per autoclave	%	0.01	max. 0.8

3.1.4 Ground granulated blast furnace slag

Blast furnace slag with specific gravity equal to 2.8 was used in concrete mixture.

3.2 Concrete Mixtures and specimen preparation.

Concrete was prepared using a planetary mixer with a capacity of 100 litres. The ingredients were put into the mixer in the decreasing order of their sizes staring from 20mm aggregate to cement. Dry mixing of the aggregates and cement was done for two minutes and then water was added gradually in the rotating mixer and allowed to mix for 5 minutes. During the mixing process, the walls and bottom of mixer were scraped well to avoid sticking of mortar. After this, the slump was checked and noted down to ascertain the effects of differently proportioned blends on workability of concrete. Finally the fresh concrete was placed in oiled moulds and compacted properly in three layers, each layer being tamped 25 times using a tamping rod. After the initial setting of concrete, the surface of the specimen was finished smooth using a trowel. The concrete specimen in the moulds were then removed after 24 hours and kept in water bath for the required curing period.

3.2.1 Mixture proportioning

The mix design procedure given in IS 10262 was followed with minor modification for M35 grade. For a target mean strength of 35 MPa and durability considerations, the water/cement ratio was fixed at 0.43 (from Fig 2, curve E IS 10262-1982 for 53G). Taking into considerations, the minimum requirements for cement content in kg/m^3 of concrete for M 35 as per IS 456-2000 is 300 kg/m^3, cement content was fixed at 380 kg/m^3. Using this, the water content was determined. In the concrete mixture fine aggregate were taken as 40% of the total aggregate volume fraction. The weights of fine and coarse aggregate were then calculated considering the specific gravities of coarse and fine aggregate.

Concrete mixtures were produced by replacing 70% of cement with fly ash and slag. Concrete mixtures labelled M1 through M7 were produced with varying contents of slag and fly ash. Proportions of GGBFS and fly ash were varied from 0% to 70% each as shown in Table 11In each mixture, 70% cement by weight was replaced by fly ash and slag. The final batch weights of the different mixes used in the study are shown in Table 12.

Table: 11 Proportion of mixes.

Name of the mix	Cement content	Slag content	Fly ash content
Control, C	100%	0%	0%
Mix M1	30%	35%	35%
Mix M2	30%	70%	0%
Mix M3	30%	10%	60%
Mix M4	30%	60%	10%
Mix M5	30%	20%	50%
Mix M6	30%	50 %	20%
Mix M7	30%	0%	70%

Table : 12 summary of materials used in various mixes

MaterialsKg/m^3	**C**	**M1**	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**
Cement 53 grade	380	114	114	114	114	114	114	114
Flyash NTPC	0	133	0	228	38	190	76	266
GGBF Slag	0	133	266	38	228	76	190	0
water	199.246	199.246	199.246	199.246	199.246	199.246	199.246	199.246
20 mm	650.730	650.730	650.730	650.730	650.730	650.730	650.730	650.730
10mm	433.384	433.384	433.384	433.384	433.384	433.384	433.384	433.384
Manufactured Sand	719.040	719.040	719.040	719.040	719.040	719.040	719.040	719.040
Total	2382.40	2382.40	2382.40	2382.40	2382.40	2382.40	2382.40	2382.40

3.3 Test Methods

In the first part, a total of eight mixes were produced and compressive strength was measured at 1, 7, 14, 28, 56 and 90 days using 150 mm cubes. The compressive strength testing was done using universal compression testing machine wherein the load was applied gradually at the rate of 400 kg/min.

3.3.1 Thermo Gravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) was performed on cement samples at different ages. TGA wasused to determine the evaporable water content, the non-evaporable water content and the $Ca(OH)_2$ contents of hydrating cementitious materials at different ages after casting. The temperature profile prescribed consisted of initially ramping the temperature from the ambient to 100 deg C at the rate of 10C/min. The samples were held at 100 deg C for 4 hours before ramping the temperature at 10degC/min to 1000 deg C. The sample was held at 1000 degC for 1 hour. Following is the profile for TGA used in the experiment.

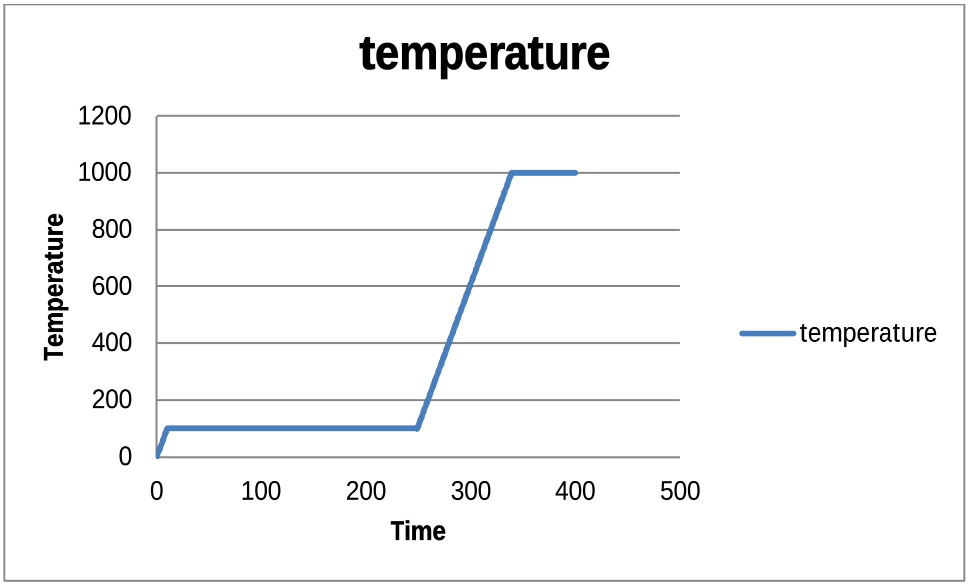


Figure: 3.1. program of TGA employed in the experiments

The TGAsamples were prepared from blended pastes of cement, slag and fly ash in the same proportion and the same water/cementitious material ratio as it was in the concrete mixes. The samples produced were kept in 5ml air tight vials so as to keep the moisture intact within the sample. At the time of testing, the samples were crushed into powder state and immediately kept into the crucibles of TG equipment to avoid any loss of moisture. The TG equipment instantaneously measures the weight of powder put for testing which was noted down precisely. From the data of TG analysis, the numerical derivative was determined from which the derivative curve was plotted using excel. The idea was to trace the peaks to determine the abrupt change in the percent mass loss curve which in turn reflects the Portlandite content in the paste.

Chapter 4

High Volume Slag-Fly Ash Ternary Blends

4.1 Introduction

Supplementary cementing materials (SCMs) are commonly employed to improve specific aspects of concrete performance. Incorporating a single SCM to improve concrete'srheology or a specific durability property does not provide a complete solution.Blended cements, which are essentially binary blends of cement and SCMs have been used and well explored. However, the use of one SCM may not provide the required performance characteristics. Every SCM mayhavelimitations associated with its use (depending on theSCM), such as, low early age strength, extended curing periods,increased admixture use, increased plastic shrinkage cracking,and freeze/thaw scaling in the presence of deicer salts. Insome instances, using a single SCM to address one durabilityconcern may result in reduced performance due to another.

While binary blends improve specific aspects of performance, the overall performance is not improved since other properties are compromised. For instance, silica fume is known to provide enhanced strength gain and reduced permeability, however, is extremely prone to restrained shrinkage cracking. Silica fume, especially in low water to cement systems produces autogeneous shrinkage and has a very high heat release. Similarly, it is shown that fly ash reduces potential for restrained shrinkage cracking, but its low reactivity is a major hindrance to the development of concrete consisting of large volumes of fly ash. It is increasingly becoming evident that use of single SCM is not sufficient. The solution lies in using ternary blends where the beneficial effects of one or more SCMs can be harnessed.The use of appropriately proportioned ternary blends allows the effects of one SCM to compensate for the inherent shortcomings of another. Such concretes have been found to exhibit excellent fresh and mechanical properties.

In this chapter the potential of high volume cement replacement with fly ash and slag is investigated. Ternary blends where 70% of cement is replaced with fly ash and slag were tested to determine the strength gain. The contribution of fly ash and slag to the strength gain are analysed. The contribution of lime to the mix by fly ash and slag in the ternary blended system are investigated using thermo-gravimetric (TG) analysis. The rate and extent of pozzoloanic reaction in the ternary blends are determined from the measured depletion of lime obtained from the TG analysis.

4.2 Experimental Results

The compressive strength obtained from the different ternary blends tested in this study are listed in Table 4.1 and shown in Figures4.1 and 4.2. The results from ternary blends containing larger quantities of Fly ash and Slag are plotted separately to facilitate comparison. The values obtained from the control mix are also shown for reference in both graphs. It can be seen that the compressive strength of the control mix exceeded the mean target strength by 28 days. The trends in strength gain suggest the possibility of further improvement in strength even after 90 days of age. The compressive strength obtained from all the ternary blends were lower than the control mix at all ages. None of the ternary blends attained the characteristic strength even after 90 days. In general, the mixtures containing slag exhibited higher strength than the mixtures containing fly ash. The mixtures containing slag (M2, M4, and M6) developed compressive strength equal to or higher than the characteristic strength of 35 MPa. In mixtures containing slag, there is no improvement in compressive strength beyond 35% replacement level.

Table 4.1: Strength of ternary blend mixes at different ages (in MPa)

days	C	M1	M2	M3	M4	M5	M6	M7
1	22.	5.65	5.74	4.69	4.73	4.92	5.74	5.20
7	39.63	18.12	22.31	12.9	21.19	15.22	13.9	10.01
14	44.48	24.91	23.09	14.7	22.48	18.61	19.84	14.9
28	48.04	29.52	30.6	20.4	29.19	23.5	26.4	19.48
56	52.4	37.93	36.77	24.88	33.05	30.5	28.28	21.36
90	54	38.69	38.31	29.14	37.45	33.48	37.47	24.46

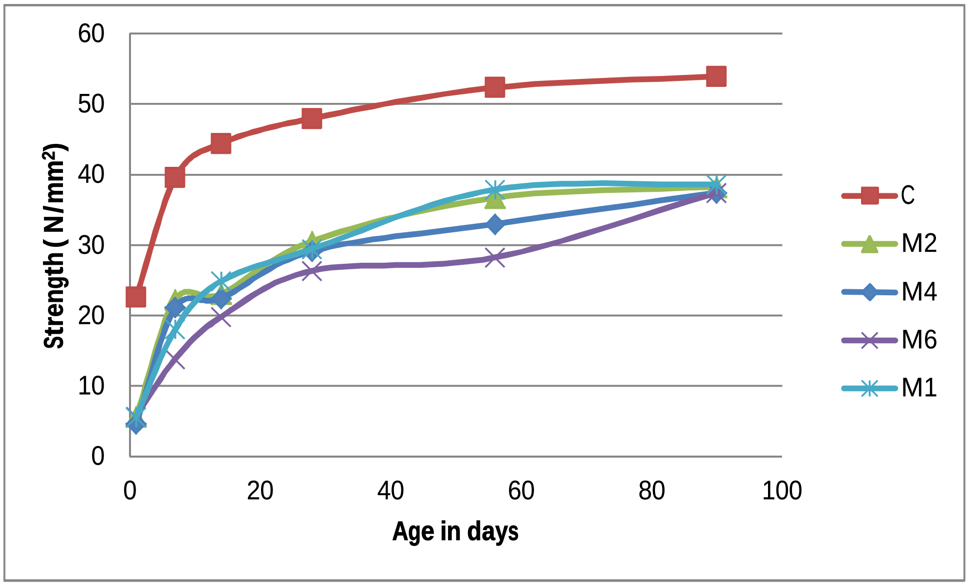


Figure 4.1: Gain in strength of ternary blends containing higher quantities of slag

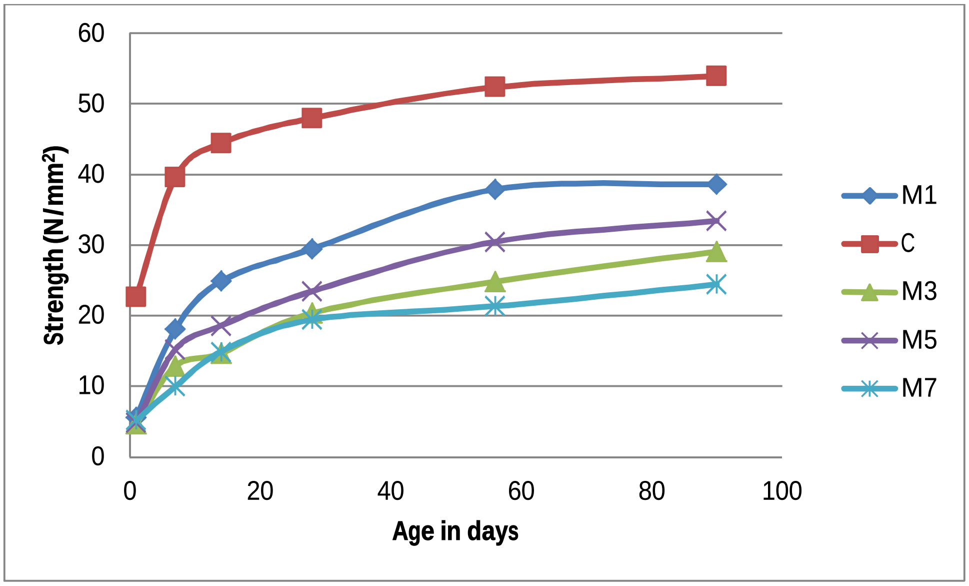


Figure 4.2: Gain in strength of ternary blends containing higher quantities of slag

Observations

To better understand the rate of strength gain and the efficiency of the supplementary cementitious material, the compressive strength of each mix at any given age was normalized with respect to the compressive strength of the Control mixture as shown in Table 4.2. It can be seen that at one day of age, the compressive strengths of all mixtures with cement replacement (M1 through M7) were roughly proportional to the percentage of cement contained in a unit volume of the cementitious material. The mixes with higher slag content, M2, M4 and M6 achieved 70% strength of the control mix by 90 days. There is no significant difference in the strength if the quantity of slag exceeds 35% of the total cementitious material in the ternary blend. The results from the fly ash indicate that even at a later age, the strength appears to be roughly in proportion to the cement and the slag content. The fly ash does not appear to be making any noticeable contribution to strength gain in the system. The general trends in compressive strength gain from all ternary blends suggest the possibility of further gain even after 90 days.

The strength of all the fly ash systems is higher than the strength obtained by considering the contribution of cement alone ie. if the fly ash were treated as inert and unreactive. Analysis of the fly ash blends indicates that the compressive strength increases with the proportion of slag in the system. If mix M7, which has 70% fly ash and no slag is treated as the baseline mix for fly ash systems, then the compressive strength improves with an increase in the proportion of slag. This clearly suggests that slag is more reactive and has a higher efficiency than fly ash. The reactivity of fly ash used in the study appears be low. The contribution to strength gain from the fly ash appears to be from the pozzolanic reaction, which would depend upon the lime released by cement hydration. The composition of fly ash suggests very little lime in the material to support hydraulic activity.

The strength of all the slag systems is higher than the strength obtained by considering the contribution of cement alone ie. if the slag were treated as inert and unreactive. The slag is clearly contributing to the strength gain from an early age. If mix M2, which has 70% slag and no fly ash is treated as the baseline mix for slag systems, then the compressive strength does not appear to show any significant change with a decrease in the slag content up to 35%. This suggests that beyond 35% the addition of slag does not contribute to strength gain. The rapid increase in the strength gain in the early ages exhibited by the slag mixes suggests hydraulic activity from the slag.

Table 4.2: Strength of various samples (in MPa) at different ages as a percentage of control mix strength

Age	C	M1	M2	M3	M4	M5	M6	M7
1	100	24.9	25.3	20.6	20.8	21.7	25.3	23
7	100	45.7	56.2	32.5	53.6	38.4	35.0	25.2
14	100	56.0	52	33.0	50.5	41.8	44.6	33.5
28	100	61.9	63.7	42.4	60.7	48.9	54.9	40.5
56	100	72.3	70.1	47.4	63.0	58.2	54	40.7
90	100	71.6	70.9	53.9	69.3	62	69.4	45.3

4.2.1 Results of TGA Analysis

TGA analyses were performed on paste samples made by mixing the cementitious material with water. A typical weight loss data curve is shown in Figure 4.3. The $Ca(OH)_2$ decomposition can be identified by the mass loss between 400 and 500 deg C. The quantity of $Ca(OH)_2$ can be determined from the percentage drop, which is determined using the derivative method. In the derivative method, the mass loss associated with $Ca(OH)_2$ decomposition is determined from the mass loss between points where the derivative curve is close to zero. The TGA mass loss curve between 400 and 500 deg C and the associated derivative curve are shown in Figure 4.4.

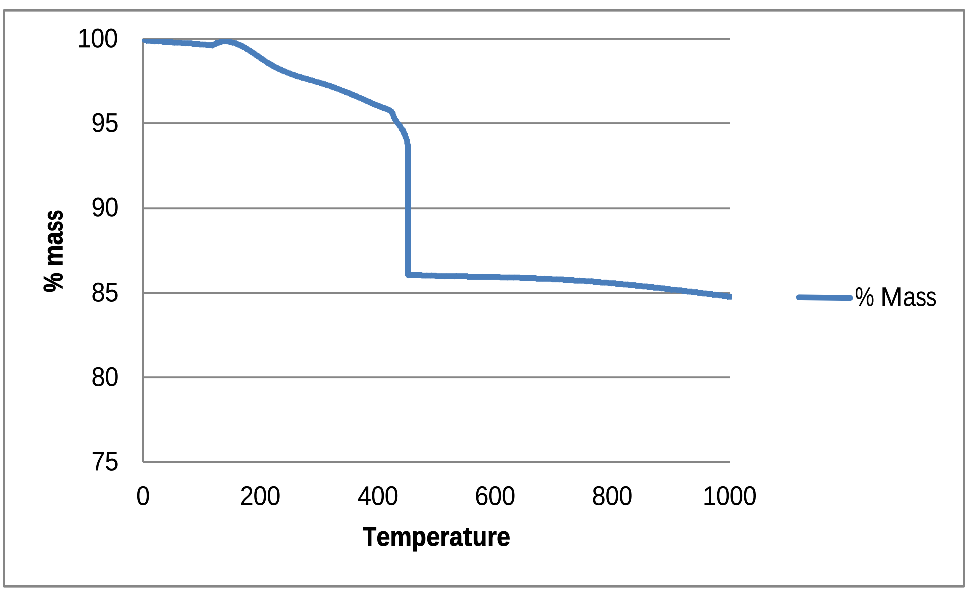


Figure: 4.3 Typical weight loss curve for M1 mix tested at 180 days for TG analysis

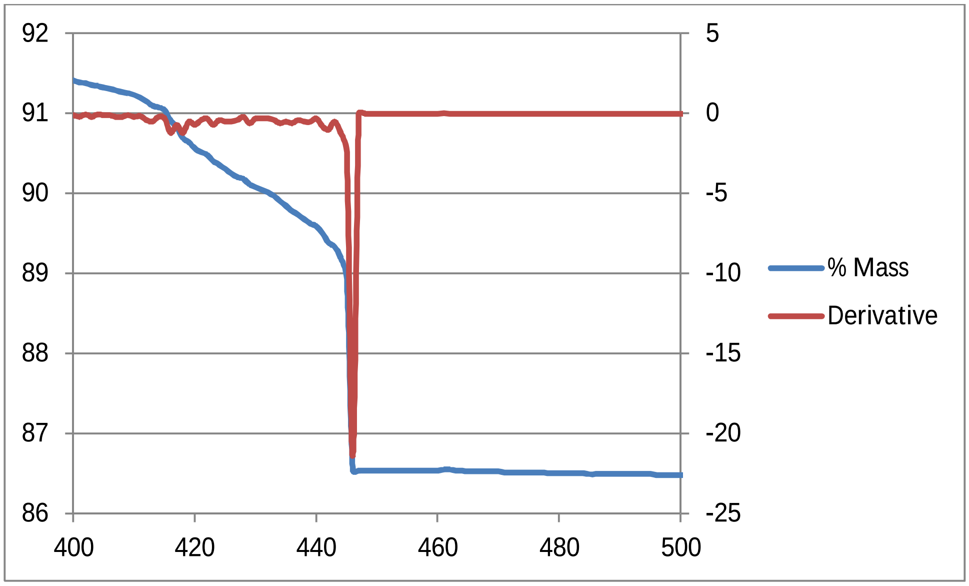


Figure: 4.4 Derivative curve for control mix tested at 28 days for TG analysis

The $Ca(OH)_2$ content of the control mix as a function of age determined from the TG analysis is shown in Figure 4.5. It can be seen that the $Ca(OH)_2$ content rapidly increases to approximately 4.4% by 14 days following which there is a negligible change with age. These findings as in agreement with the measured increase in compressive strength; the rapid increase in the $Ca(OH)_2$ content coincides with the rapid increase in strength in the first 14 days. The slowdown in the rate of strength gain after the first 14 days corresponds with the observed decrease in the rate of $Ca(OH)_2$.addition. The observations from TGA further indicate that strength gain produced by the hydraulic reaction of cement results in production of $Ca(OH)_2$.

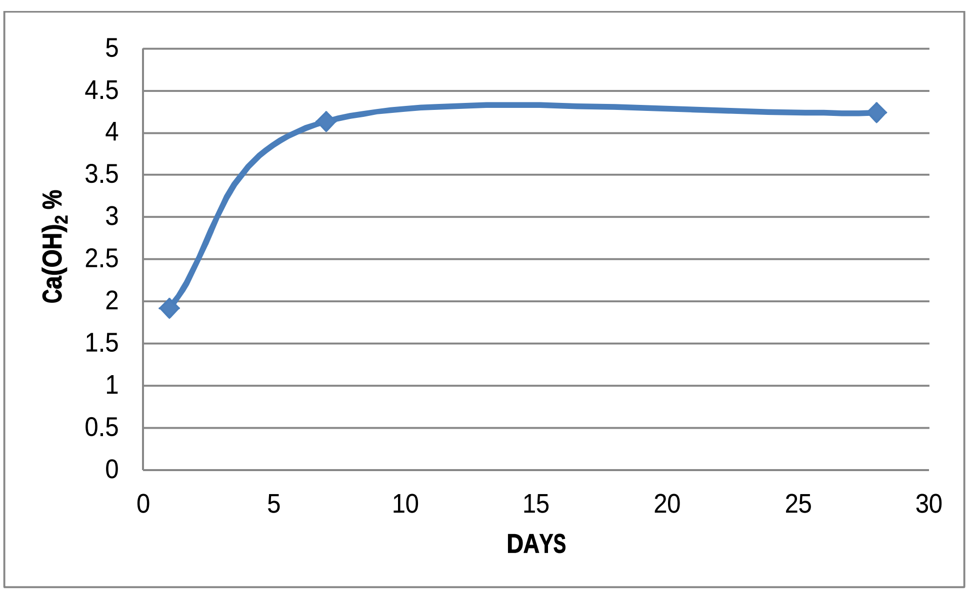


Figure: 4.5: Calcium hydroxide content for control mix obtained from TG analysis

The $Ca(OH)_2$ percentage for the slag blends are shown in Figure 4.6. The $Ca(OH)_2$ in the slag blends increase up to 28 days followed by steady decrease. The initial contribution of $Ca(OH)_2$ comes from hydraulic activity of cement and slag. Further, the $Ca(OH)_2$ content increases with an increase in content of slag. The percentage of $Ca(OH)_2$ in the slag mixes is also higher than the corresponding content in Control mix. This suggests that the additional $Ca(OH)_2$ is contributed by the reaction of slag. The depletion of $Ca(OH)_2$ after 28 days suggests pozzolanic activity. The observation from the TG analysis are therefore in compliance with the observed trends in strength gain and confirm the earlier observation that the change in the rate of strength gain is associated with the change in the mechanism of reaction which contributes to strength gain. Both slag and fly ash contribute the depletion of $Ca(OH)_2$ in the slag systems after the initial 28 days; the rate of depletion however increases with the increase in the fly ash content in the mix.

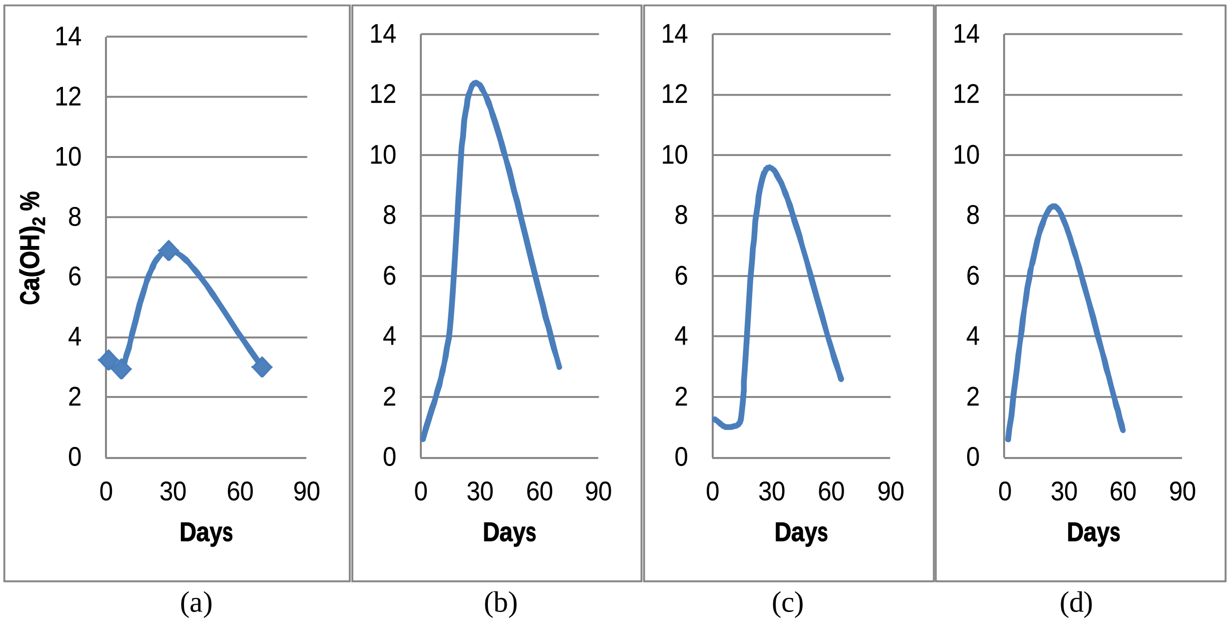
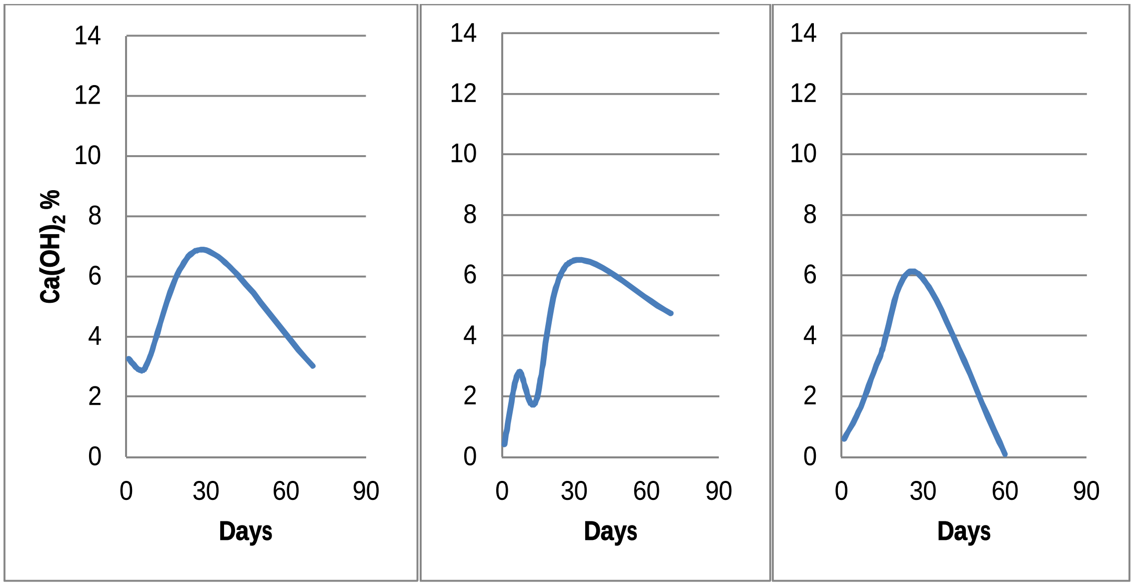


Figure 4.6: $Ca(OH)_2$ content determined from TGA for (a) M1; (b) M2; (c) M4 and (d) M6 mixes.

The results of TGA for the fly ash mixes are shown in Figure 4.7. It can be seen that trends are similar to those observed in slag mixes. There is an initial increase in the $Ca(OH)_2$ up to 28 days followed by depletion. Comparing control mix with the baseline fly ash mix reveals additional $Ca(OH)_2$ in the system with fly ash. This suggests that fly ash is responsible for contributing $Ca(OH)_2$ in the cementitious mix. The rate of depletion of $Ca(OH)_2$ after the first 28 days is the most rapid in mixes containing higher fly ash content. The complete depletion of lime in the M7 mix suggests there is insufficient lime to completely react with the available reactive silica in fly ash.



(a) **(b)** **(c)**

Figure 4.7: $Ca(OH)_2$ content determined from TGA for (a) M1; (b) M3 and (c) M7 mixes.

4.3 Summary and Conclusions

Based on the results presented in this chapter the following conclusions can be drawn

- Slag contributes to strength gain at both the early and later ages.
- There is no improvement in strength when slag is more than 35% by mass of the supplementary cementitious material content.
- The low Calcium Fly ash used in this study exhibits very low reactivity. Its contribution to early age strength gain is very small.
- Both Slag and Fly ash blends exhibit a distinctive change in the rate of strength gain after 28 days, associated with a change in the mechanism which produces strength gain in the material. Results of TGA analysis indicate an increase in the $Ca(OH)_2$ content up to 28 days, following which there is a decrease in the lime content in the mix. Slag contributes to the total lime in the system up to 28 days. The contribution of lime from fly as is small. The rate of depletion of lime increases with an increase in the fly ash content. In pure fly ash system there is a complete depletion of lime.

The available results suggest the possibility of using lime to activate the blends. This is investigated in the next chapter.

Chapter 5

Lime Activation of High Volume Cement Replacement of Ternary Blends

5.1. Introduction

High volume replacement of cement with supplementary cementitious materials (SCM) has been shown to impact the strength gain and the final strength of concrete. Developing equivalent strength gain as cement is often called the efficiency of the SCM. While slag has been has been shown to provide better long-term performance and even strength, fly ash at high replacement levels suffer from severe loss in strength. Researchers have tried mechanical, thermal and chemical methods of activation to achieve faster strength gain and higher ultimate strength of the SCM. The activation methods rely on grinding the SCM to a smaller particle size, increasing temperature and using chemical activators to increase the reactivity and hence the rate of strength gain and ultimate strength.

The potential for contributing to overall strength depends upon the reactive silica content in the SCM. Grinding and thermal activation are ineffective when the chemical species present do not favour a reaction. The use of chemical activators has been very effective in activation of potential cementitious property of blast furnace slag and pozzolanic reactivity of pozzolans.The use of lime, in particular, has been shown to be effective and efficient technique to activate the potential pozzolanic reactivity of coal fly ashes and to improve the properties of the fly ash concrete. Previous studies on lime activation have considered low volume cement replacements.

In this study, lime activation has been studied in high volume cement replacement blends. Strength gain was monitored in concrete mixtures with different levels of lime dosage. Three baseline concrete mixtures where 70% of the cementitious material consisted of SCMs were selected for evaluation. The SCMs in these mixtures were replaced with equal mass of lime at different proportions. The results obtained from lime replacement were interpreted considering two effects: (a) reduction in the reactive silica in the mixture with the decreasing SCM content; and (b) the gain in strength contributed by the activation provided by lime.

5.2. Experimental Program

Three concrete mixtures were chosen to evaluate the influence of lime dosage on the compressive strength gain. In each mix, the SCM were replaced with equal weight of lime; in the M1 mix the two SCMs were replaced in equal proportion. In all mixtures the cement content was kept constant. Three different levels of lime replacements corresponding to 5, 10 and 15% of the total cementitious material were evaluated. The mix designations for the different levels of cement replacement are shown in Table 5.1. For each mix compressive strength was measured at 1, 7, 14, 28, 56 and 90 days of age using 70.6mm cubes.

Table 5.1: Concrete mix designations for different lime replacement levels

MIX	**Proportion**
Control C	100% cement
M1-C	30+35+35 with 0% lime
M1-5P	30+35+35 with 5% lime
M1-10P	30+35+35 with 10% lime
M1-15P	30+35+35 with 15% lime
M2-C	30+70+0 with NO lime
M2-5P	30+70+0 with 5% lime
M2-10P	30+70+0 with 10% lime
M2-15P	30+70+0 with 15% lime
M7-C	30+0+70 with NO lime
M7-5P	30+0+70 with 5% lime
M7-10P	30+0+70 with 10% lime
M7-15P	30+0+70 with 15% lime

5.3. Results and Analysis

The compressive strengths achieved by the different mixes as a function of age are shown in Table 5.2. Compressive strength results of lime replacement on the slag blend M_2 are shown in Figure 5.1. The results indicate that lime has little or no influence on the performance of slag. In each mix, which contains lime, the quantity of lime is exactly equal to the weight of slag removed from the mix. The compressive strength results indicate that the gain strength obtained as a result of activation provided by lime exactly balances the loss of strength gain produced by the hydraulic action of slag.

Table 5.2: Compressive strength as a function of age in lime activated systems

	Strength in N/mm2												
days	C	M1-C	M1-5P	M1-10P	M1-15P	M2-C	M2-5P	M2-10P	M2-15P	M7-C	M7-5P	M7-10P	M7-15P
1	18.05	8.1	5.8	7.45	6.39	8.4	9.87	9.03	11.16	1.87	5.13	4.61	2.27
7	21.77	14.07	11.86	14.55	13.13	17.76	13.51	16.03	20.17	8.55	19.99	9.44	11.67
14	33.14	23.26	21.88	18.98	20.2	22.45	21.14	23.15	16.24	10.57	26.07	10.79	18.45
28	38.27	29.6	29.71	27.97	22.24	25.28	27.89	27.5	23.13	13.23	30.82	16.83	21.14
56	40.91	29.6	30.88	29.1	23.79	36.79	31.57	30.52	28.88	23.18	30.85	23.51	21.95
90													

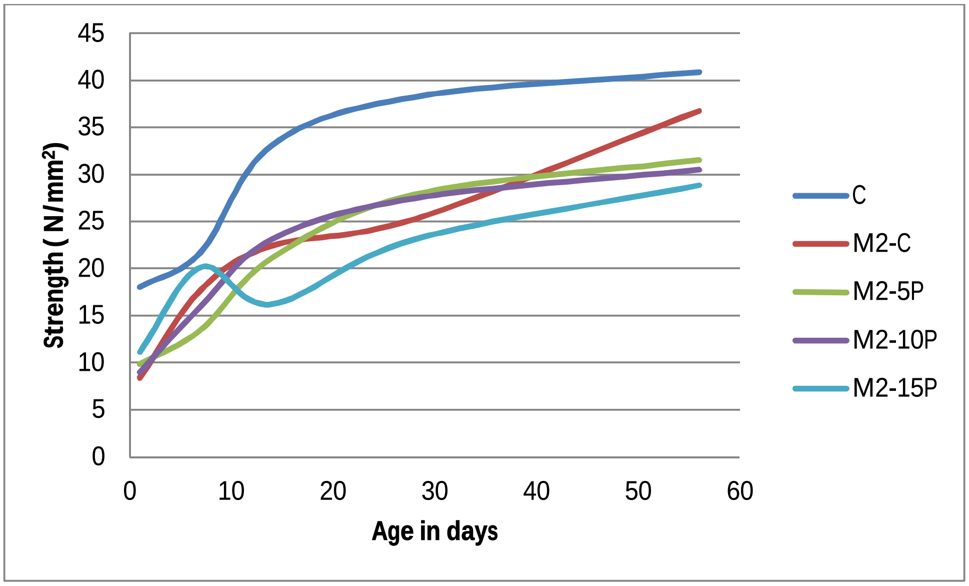


Figure 5.1: Compressive strength gain in lime activated M2 mix with 70% slag and 30% cement.

Results from Mix M1 are shown in Figure _. The results indicate that the lime activation has little or no influence on the compressive strength gain on the ternary blend up to 10% lime dosage. Increasing the lime dosage to 15% impacts the long-term strength obtained at 90 days. The results indicate that the loss in the contribution from the hydraulic and pozzolanic activities of fly ash and slag is exactly balanced by the gain in strength achieved by the lime activation. The results of slag previously indicated that the lime replacement of slag provided exact equivalence in strength. The results here indicate that fly activated by the presence of lime up to 5% lime dosage.

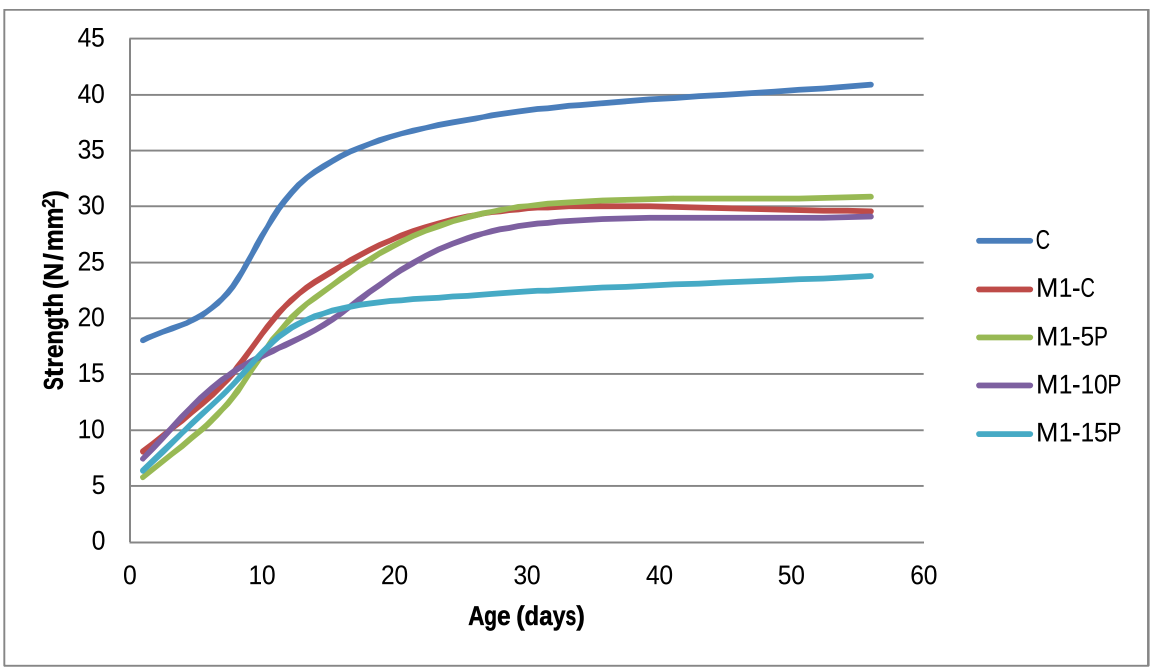


Figure 5.2: Compressive strength gain in lime activated M_1 mix with 35% slag, 35% fly ash and 30% cement.

Results from Mix M7 which contains 70% fly ash and 30% cement are shown in Figure 5.3.Results from fly ash indicate that fly ash is effectively activated upto a lime dosage of 5%. There is clearly an improvement in the strength exhibited by the M7 mix with 5% replacement of SCM with lime. On increasing the lime replacement beyond 5% there is a decrease in strength when compared with the 5% replacement. There is however an increase in strength exhibited by lime activated M7 mix up to 10% replacement when compared with the baseline M7 mix.

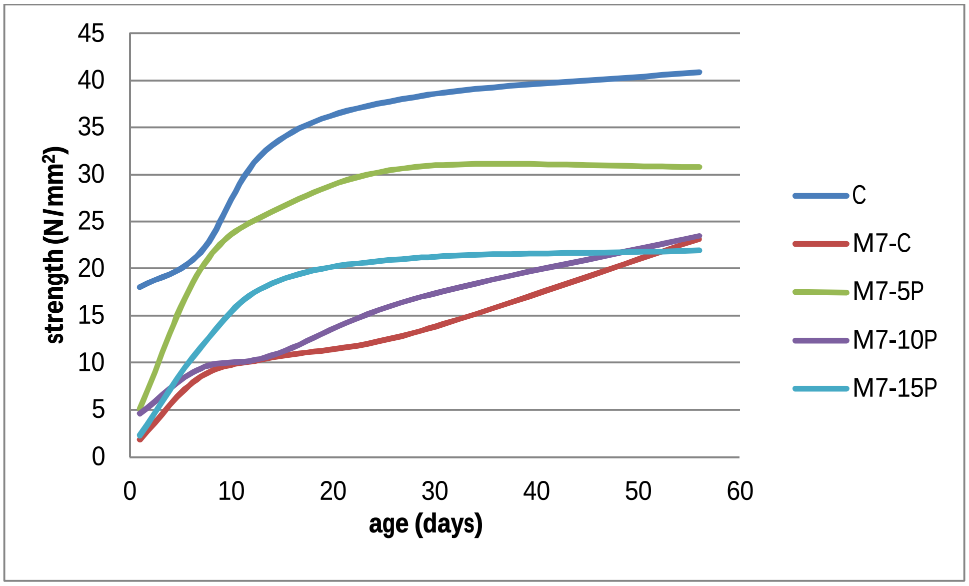


Figure 5.3: Compressive strength gain in lime activated M7 mix with 70% fly ash and 30% cement.

5.4. Discussion

The results obtained in this study can now be analyzed in the context of available information in the literature. Fly ash reacts with the lime released from the hydration of Portland cement to form calcium silicate hydrate (C-S-H) with a low CaO/SiO_2 ratio and calcium aluminate hydrates. The pozzolanic reactions between fly ash and lime are very slow. It is estimated that the reaction degree of fly ashes is only about 20% at 90 days, compared with 80% for Portland cement. Due to the pozzolanic reactions between lime and fly ash, the free lime content in fly ash cement or concrete decreases with time depending on the content and nature of the fly ash in the cement or concrete. Also, the CaO/SiO_2 ratio of C-S-H in fly ash cement or concrete is also lower than that in Portland cement [Regourd 1987].

The addition of industrially produced quicklime on fly ash–Portland cement pastes has been shown to have a positive influence mainly on the strength development and reaction rate of high lime fly ash. It was demonstrated that replacing a small amount of a Class C fly ash with quicklime resulted in a notable acceleration of the fly ash degree of reaction throughout the curing period. Apart from the physical effect of lime and the creation of CH bonds among ash particles, quicklime addition increased the solubility of SiO_2 leading to a greater release of soluble silica into the hydrating matrix. Conversely, when quicklime replaced an ash of lower lime content, activation was limited to the early stages of hydration.

The results of lime activation indicate a clear improvement in the strength from fly ash, which suggests the reactive silica in fly ash undergoes reaction in the presence of lime. The results indicate a larger relative increase in the early age, while the later age strengths are not significantly improved. This is in agreement with the previous research findings. Therefore, there is a contribution to strength from reaction other than the pozzolanic reaction, which is known to be slow. The reduction in the strength on increasing the lime content beyond 5% suggests that excess lime may impede the solubility of SiO_2.

5.5. Conclusions

Based on the results presented in this chapter the following conclusions can be drawn:

- Experimental evidence suggests that 5 to 10 % lime addition has a significant effect on fly ash systems. There is clearly an improvement in the early age strength of all the mixes of fly ash.
- There appears to be an optimum lime replacement level for achieving highest strength in fly ash mixtures. While both 5 and 10% lime replacement produced improvements in strength gain over the unactivated fly ash mix, the strength obtained from the 10% mix was lower than the 5% mix.
- There is no noticeable change of chemical activation on any of the slag systems at thee replacement levels of lime above 5% of slag content.

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